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Recent Advances in High Temperature Electrolysis at Idaho National Laboratory: Single Cell Tests

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RECENT ADVANCES IN HIGH TEMPERATURE ELECTROLYSIS AT IDAHO NATIONAL LABORATORY: SINGLE CELL TESTS

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ABSTRACT

An experimental investigation on the performance and durability of single solid oxide electrolysis cells (SOECs) is under way at the Idaho National Laboratory. In order to understand and mitigate the degradation issues in high temperature electrolysis, single SOECs with different configurations from several manufacturers have been evaluated for initial performance and long-term durability. A new test apparatus has been developed for single cell and small stack tests from different vendors. Single cells from Ceramatec Inc. show improved durability compared to our previous stack tests. Single cells from Materials and Systems Research Inc. (MSRI) demonstrate low degradation both in fuel cell and electrolysis modes. Single cells from Saint Gobain Advanced Materials (St. Gobain) show stable performance in fuel cell mode, but rapid degradation in the electrolysis mode. Electrolyte-electrode delamination is found to have significant impact on degradation in some cases. Enhanced bonding between electrolyte and electrode and modification of the microstructure help to mitigate degradation. Polarization scans and AC impedance measurements are performed during the tests to characterize the cell performance and degradation.

INTRODUCTION

Large-scale hydrogen production is the most important factor that impacts the hydrogen economy. An estimation of 53 million metric tons of hydrogen was produced in 2010 globally. An annual growth rate of 5.6% was forecasted during 2011-2016 [1]. However, most hydrogen produced is from fossil fuels, including natural gas, oil, and coal [2]. Non-fossil based large-scale hydrogen production gain growing interest all over the world. High temperature electrolysis (HTE) is one of the most efficient technologies to produce carbon-free hydrogen in large scale [3]. INL has demonstrated HTE at the 15 kW scale with a hydrogen production rate in excess of 5000 NL/hr [4]. However, technical barriers need to be resolved before commercialization of HTE technology. The major issue for HTE is long-term performance degradation of the solid oxide electrolysis cells (SOECs) [5-8]. Although common solid oxide fuel cells (SOFCs) can be reversely operated in electrolysis mode, they usually exhibit much higher degradation rates in the electrolysis mode than in fuel cell mode [9-10]. In our previous stack tests, air electrode delamination, Cr vapor poisoning, microstructure degradation, and seal leakage were found to significantly affect the durability of the stack [11-12]. To understand the degradation mechanism and develop SOECs for strong durability, more single cell tests are needed.

Compared to the stack tests, the investigation on the degradation issues were only focused on single cell level in this paper. A new experimental apparatus was developed for single cell tests. SOECs obtained from Ceramatec, MSRI, and St. Gobain were investigated experimentally. Initial performance and long term durability tests were conducted in both the fuel cell and electrolysis modes of operation. Improved durability were found on Ceramatec and MSRI single cells, while St. Gobain cells showed unsatisfied performance in the electrolysis mode.

MATERIALS AND EXPERIMENTAL APPARATUS

The state-of-the-art SOECs were provided by Ceramatec Inc., Materials and Systems Research Inc. (MSRI), and Saint Gobain Advanced Materials (St. Gobain). The common materials used in Ceramatec SOECs are ScSZ electrolyte, Ni-Ceria steam/hydrogen electrode, and La-Co-Fe oxide based perovskite air electrode. Ceramatec SOECs are electrolyte-supported button cells with 2.25 cm^2 active area. Both MSRI and St. Gobain SOECs are Ni/YSZ-supported cells with 8YSZ

electrolyte. LSCF is used as the air-electrode material in MSRI SOECs, while in St. Gobain cells both modified LSM and LSCF are used. All of the electrode-supported SOECs are square, 5 × 5 cm in dimension with 16 cm^2 active area. MSRI SOECs were fabricated using their state-of-the-art fabrication processes, and the microstructure of the cells was optimized specifically for operation in the electrolysis mode. St. Gobain SOECs were actually traditional SOFCs, and were optimized for long term operation in the fuel cell mode.

A newly developed cell fixture was used to tested MSRI and St. Gobain SOECs, as shown in an exploded view in Fig. 1. There are a few advantages of this apparatus for the fuel cell and electrolysis tests. First, it is versatile and robust. It can be used for both single cell and short stack tests. So far thirteen single cells and two 3-cell short stacks have been tested on this apparatus without any post-test treatment. Second, it is designed for the operation at high current density and electrochemical measurements. Third, it eliminates the possibility of Cr poisoning. The investigation on the degradation was confined within the cell. The detailed instruction of this fixture is stated below.

A hydrogen/steam mixture is fed from the bottom through a 1/4 in coiled Inconel tube into the inlet hole in the bottom of the Hastelloy-X (HastX) base plate. The flow then passes through a slot at the bottom of the Alumina cell holder. A mica/glass cell gasket is placed between the cell holder and the nickel plate for sealing. The nickel plate works as the current collector for the steam electrode. A corrugated nickel flow field is used for managing the hydrogen steam flow and for electric conduction. A nickel felt is placed between the electrode and the nickel flow field to minimize the electrode/flow field contact resistance. The Ni felt and flow field are trimmed to fit the size of the Ni plate sitting in the recess of the cell holder. After passing along the bottom of the cell, the flow exits through another slot and vents out via a 3/8 in inconel tube. The outlet tube is sized larger than the inlet tube to minimize the back pressure on the cell seal.

On the air side of the cell, a gold-plated perforated inconel plate is used as the current collector and air flow distributer. Air is introduced through a tube that is welded to the inconel plate. Air flow is distributed along the air side of the cell through an array of flow channels milled into the bottom of the inconel plate. Air exhaust gas vents out to the furnace. A gold mesh is placed between the air electrode and the plate to minimize ohmic loss and to further improve air flow distribution. The top conductor / air flow distributor consists of three parts. The tube is welded and protruded slightly into the center hole of the upper inconel plate. Another inconel plate was machined with the flow channels and through-plate holes. These two plates were then welded together. Gold plating was applied to the inconel surfaces that are exposed to the furnace hot zone to minimize oxidation.

A fixed compression load is applied to the solid oxide cell by means of weights, as shown in the test stand overview, Fig. 2. The load is transferred via an alumina tube from the dead weights to the top cell contact plate. This load

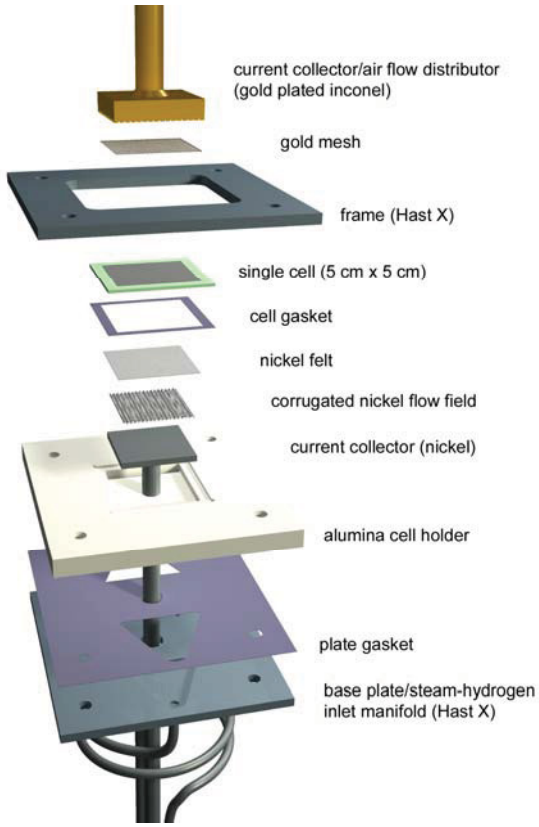

Figure 1. Exploded view of the cell fixture used for testing MSRI and St. Gobain SOECs.

simultaneously compresses the cell against the nickel felt, flow field and current collector on the bottom steam/hydrogen side of the cell and against the gold mesh on the air side. It also compresses the cell against the seal around the outer edge of the cell which rests on the shelf milled into the alumina cell holder. The HastX weight plates are held in alignment outside of the furnace by the upper portion of the threaded rods which extend upward for this purpose.

The compressive load can also be applied by means of springs. Spring loading is more compact and easier to implement than adding weights. Spring loading was used in all of the MSRI SOEC tests, because different loads were required for curing process. Dummy weights were used in the St. Gobain SOEC tests due to a constant loading requirement for curing process.

A photograph of the test stand installed in the furnace base for testing St. Gobain SOECs is shown in Fig. 3. Note that the upper part of the alumina load transfer tube is located outside of the furnace. So the weights stay outside of the hot zone. Holes were drilled in the bottom of the kiln for pass-through of the flow tubes, the alumina spacer rods, the nickel current collector rod and instrumentation.

A photograph of the test stand installed in the furnace base is shown in Fig. 3. Note that the upper part of the alumina load transfer tube is located outside of the furnace. So the weights

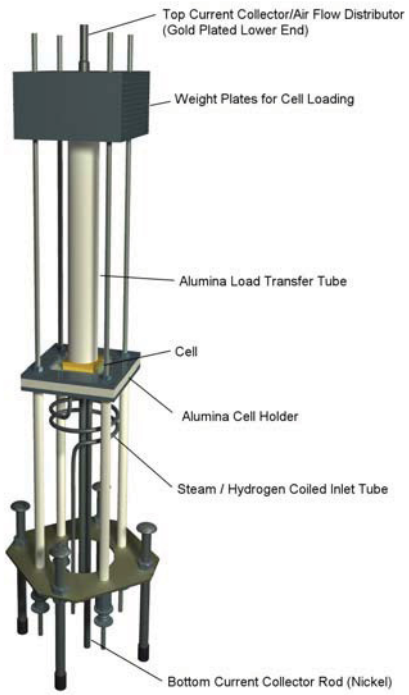

Figure 2. Test stand overview.

stay outside of the hot zone. Holes were drilled in the bottom of the kiln for pass-through of the flow tubes, the alumina spacer rods, the nickel current collector rod and instrumentation.

AC impedance spectroscopy is used to characterize the electrochemical behavior of the SOECs. Impedance measurements are obtained using a Solartron Modulab 2100A system. Impedance data are obtained in fuel cell mode, electrolysis mode, and open circuit condition. During the long term tests, impedance measurements are conducted periodically to characterize the degradation of the cells.

A piping and instrument diagram (P&ID) for the experimental apparatus used for MSRI and St. Gobain single cell testing is presented in Fig. 4. Primary components include gas supply cylinders, mass-flow controllers, a heated water-bath humidifier, on-line dew point sensors, temperature and pressure measurements, high temperature furnace, and the solid oxide electrolysis cell. Nitrogen is used as an inert carrier gas. Inlet flow rates of nitrogen, hydrogen, and air are established by means of precision mass-flow controllers. Hydrogen is included in the inlet flow as a reducing gas in order to prevent oxidation of the Nickel cermet electrode material. Air flow to the cell is supplied by the shop air system, after passing through a two-stage extractor / dryer unit. The hydrogen-side inlet gas mixture, consisting of hydrogen and nitrogen is mixed with steam by means of a heated humidifier. The dew point temperatures of the nitrogen / hydrogen / steam gas mixture exiting the humidifier and downstream of the cell are monitored

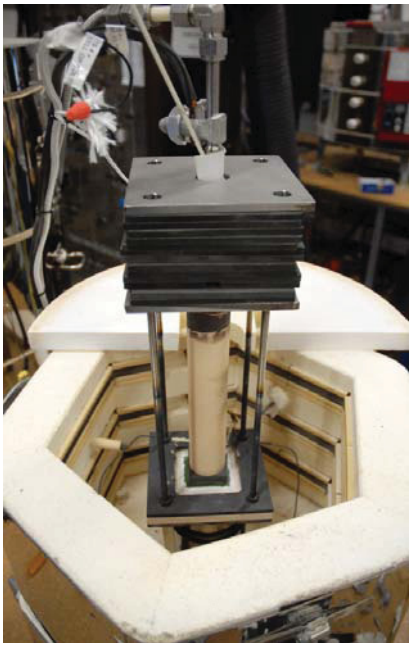

Figure 3. Single cell test stand installed in furnace.

continuously using a precision dew point sensors. All gas lines located downstream of the humidifier are heat-traced in order to prevent steam condensation.

The P&ID for Ceramatec button cell testing is similar as Fig.4 except that an alumina tube is used as a cell holder. The button cells were placed onto the end of the alumina tube and sealed by ceramic sealant. The hydrogen/steam electrode is exposed to the hydrogen and steam flowed inside the tube, while the air-side electrode is exposed to the ambient atmosphere in the furnace. Platinum gazes are attached on both sides of the button cells for current collection.

TEST PROCEDURE

Each single cell undergoes three steps during the test, including initial heatup and cell reduction, performance characterization, and long-term testing. During cell reduction, nickel oxide in the steam/hydrogen electrode is reduced to nickel metal by slowly introducing a dry hydrogen flow. Initial cell performance is evaluated by mean of a series of voltage-current (V-I) sweeps with different steam content at the steam/hydrogen inlet.

After the performance evaluation, the cell is operated in long term mode. MSRI and St. Gobain SOECs are operated in the fuel cell mode and the electrolysis mode, which is also called as the reversible mode. Ceramatec SOECs are only operated in the electrolysis mode. The operating conditions of different SOECs during long term tests are listed in Table I. AC impedance measurements are performed following the DC sweeps as well as periodically during the long-term tests. The excitation frequency range is 100 kHz – 0.1 Hz.

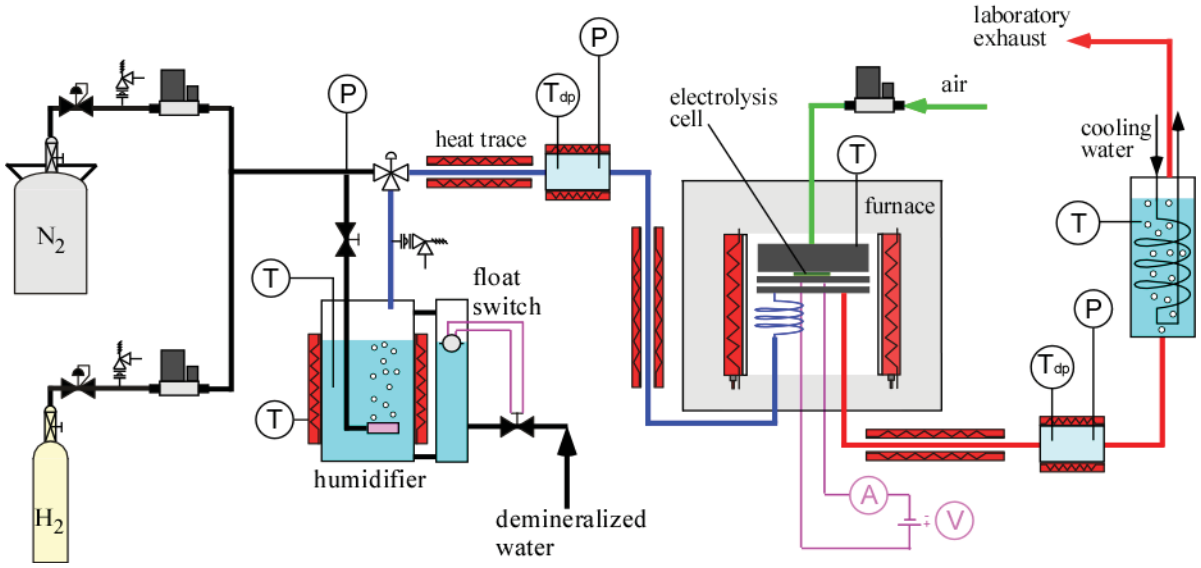

Figure 4. Piping and instrument diagram for single cell test apparatus.

Table I. Operating conditions during long term tests

Cell #	Temp °C	Flow Rate H_2/N_2/Air sccm	Dew Point °C	Control Mode
MSRI #1	800	500/500/1000	70	CC*
MSRI #2	800	500/500/1000	80	CC
St. Gobain #1	850	500/500/1000	70	CC
St. Gobain #2	850	500/500/1000	70	CC
Ceramatec #1	850	50/200/0	70	CPV**
Ceramatec #2	850	50/200/0	70	CPV

* CC means constant current

** CPV means constant power supply voltage

RESULTS AND DISCUSION

MSRI single cells

Two MSRI single cells were tested to investigate the factors that affect their durability. Fig. 5 shows the results of the initial performance characterization of MSRI #2, which is the typical initially behaviors of MSRI single cells. Those curves show the effect of the steam content on cell performance. Curves representing higher steam content show more linear trends both in fuel cell and electrolysis modes. The nonlinearity in the curves at low steam content is associated with the high sensitivity of the Nernst potential to small changes in average steam content. Also, in the electrolysis mode, higher current densities can lead to steam starvation if the average steam content is low. A high inlet dew point temperature, typically 60 °C or higher is suggested for long-term operation in the electrolysis mode [10]. The figure also shows that the ASR curves remain flat at high steam content in both modes, while becoming significantly curved especially in electrolysis mode as steam content decreases. At high steam content, the ASR values are similar in the fuel cell and

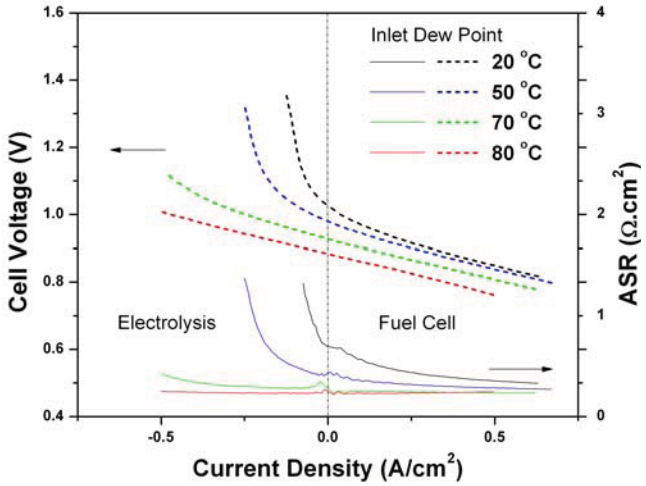

Figure 5. Polarization curves and calculated ASR values in the fuel cell and electrolysis modes of a MSRI single cell.

electrolysis modes. At 80 °C inlet dew point (56% steam content), ASR values remain below 0.25 $\Omega.cm^2$. Generally, MSRI single cells demonstrate strong initial performance both in the fuel cell and electrolysis modes.

MSRI #1 was operated in the fuel cell mode for 120 hours, followed by about 300 hour operation in the electrolysis mode. Both modes were controlled galvanostatically at 0.5 A/cm^2 in order to comparing the degradation between two modes. Fig. 6 shows the result of the long-term test MSRI #1. It is seen that this cell behaved steady during fuel cell operation with a degradation rate of 0.64%/khr. After being switched into electrolysis, the cell degraded faster than in the fuel cell mode. However, a degradation rate of 4.26%/khr at 0.5 A/cm^2 is considered as a durable SOEC nowadays.

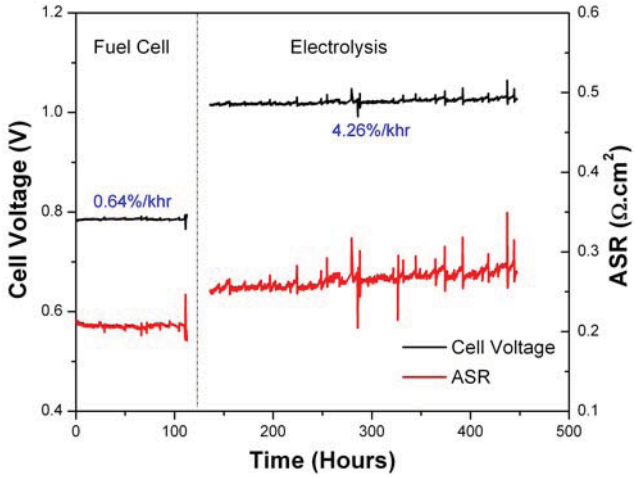

Figure 6. Long-term test of MSRI #1 in the fuel cell and electrolysis modes.

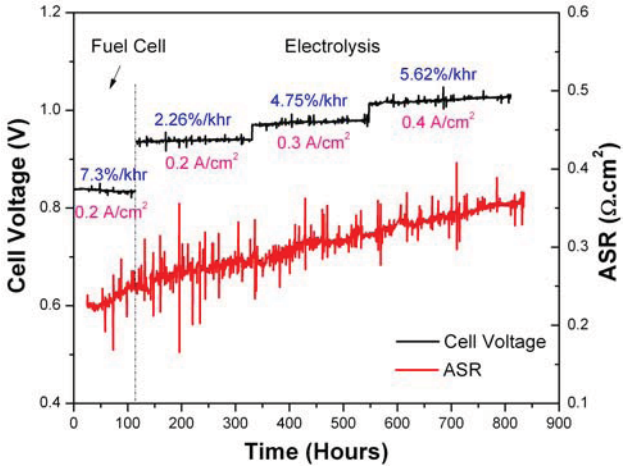

Figure 7. Long-term test of MSRI #2 in the fuel cell and electrolysis modes. The cell was operated at three different current densities in the electrolysis mode.

In order to provide information of an optimized operating condition for MSRI stack testing in the future, a different long term test was performed on MSRI #2. The cell was firstly operated in the fuel cell mode for about 110 hours, and then in the electrolysis mode it was operated at different current densities each for about 200 hours. The effect of current density on degradation is illustrated in Fig. 7. In the electrolysis mode, the cell shows the degradation rates of 2.26%/khr, 4.75%/khr and 5.43%/khr at 0.2 A/cm^2, 0.3 A/cm^2, and 0.4 A/cm^2, respectively. It clearly demonstrates that degradation rate increases as current density increase. Nevertheless, MSRI SOECs still demonstrated excellent durability in the electrolysis mode.

Ceramatec button cells

Two Ceramatec button cells were tested to evaluate the durability of the cells with advanced air electrode in the

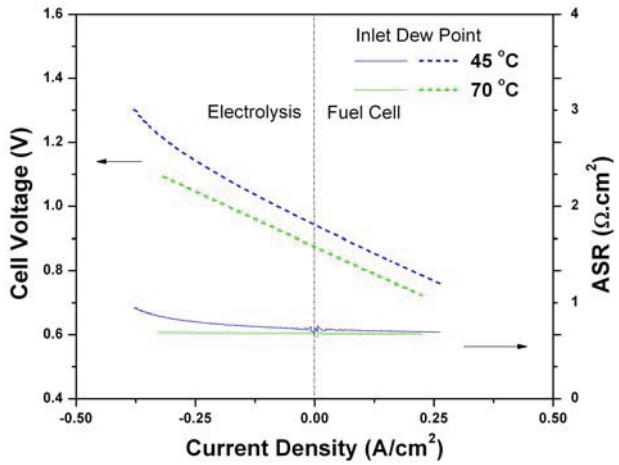

Figure 8. Polarization curves and calculated ASR values in the fuel cell and electrolysis modes of a Ceramatec #2.

electrolysis mode. Fig. 8 shows a typically initial performance of Ceramatec SOEC. Compared to the electrode-supported SOECs, the electrolyte-supported cells have much higher ASR when they are operated at the same conditions. It is mainly due to the bulk resistance of the thicker electrolyte. In the case of Ceramatec button cells, the ASR at 70 °C inlet dew point (37% steam content) is close to 0.75 Ω.cm^2 during polarization sweeps. However, both Ceramatec button cells tested at INL demonstrated exceptional durability during electrolysis.

Ceramatec #1 had been operated in the electrolysis mode for about 4000 hours and showed negative degradation (performance increasing) all the way along the test. Several power outages happened during the test and the cell did not survive after the thermal cycle caused by the power outage around 4000 hours. Fig. 9 represents the results of its long-term test. Due to the limitation of our button cell testing facility, the cell was only controlled by constant power supply voltage. Therefore the cell performance improvement is characterized by decrease of the cell voltage but increase of the current

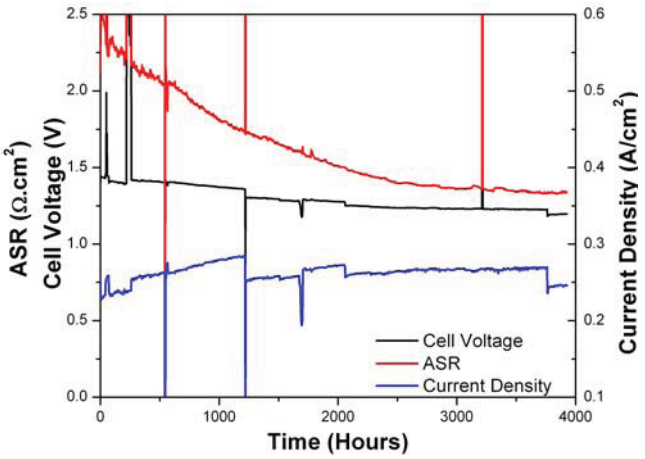

Figure 9. Long term electrolysis test of Ceramatec #1.

density. Although not continuously, the cell voltage kept decreasing for 4000 hours, while the current density kept increasing. The ASR dropped from 2.5 Ω.cm^2 to 1.4 Ω.cm^2 after 4000 hour operation. However, in terms of ASR, the performance was worse than those electrode-supported SOECs.

The durability test on Ceramatec #2 was conducted afterwards to verify if the performance of Ceramatec #1 is repeatable. Fig. 10 shows the long term durability test of Ceramatec #2. For the first 1100 hour operation, the cell degraded rapidly initially and then stabilized. The cell performance started increasing after a thermal cycle due to a

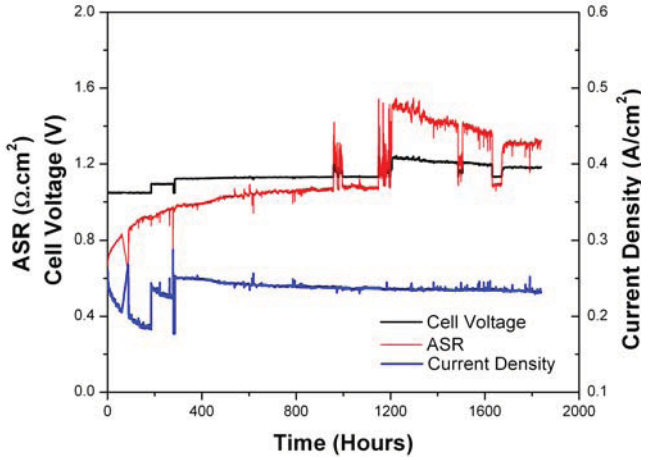

Figure 10. Long term electrolysis test of Ceramatec #2.

power outage around 1100 hours. For the following 700 hours, the ASR decreased from 1.5 Ω.cm^2 to 1.3 Ω.cm^2. The cell was shut down finally after another power outage happened at 1850 hours. Overall Ceramatec #2 did not behave similarly as Ceramatec #1.

Nevertheless, the negative degradation (i.e. performance increase) found on Ceramatec #1 is similar as what was found in the following stack test [13]. However, the observed performance increase over the long time period cannot be easily explained. More stack and button cell tests will be tested at INL to fully understand this exceptional behavior.

St. Gobain single cells

Different than the previous SOECs, the St. Gobain cells were actually developed as SOFCs. Stable performance was expected in the fuel cell mode, while its behavior in the electrolysis mode was unknown. The results of two St. Gobain single cells with different air-electrodes are reported here. Fig. 11a shows the polarization sweeps of the single cells with modified LSM (black curves) and LSCF (red curves) air electrodes at different inlet dew points. Based on the slopes of the V-I curves, the single cell with the LSCF air electrode demonstrated better performance than the one with modified LSM electrode.

Following the initial performance evaluation, the single cells were put in a long-term operation. Fig. 12 shows the result

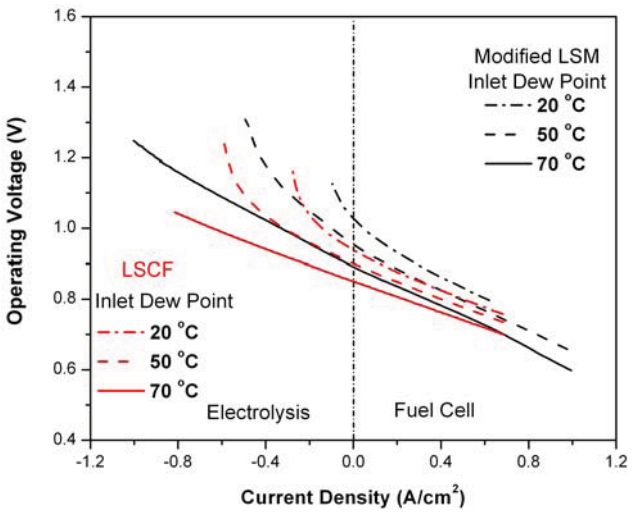

Figure 11. Polarization curves in the fuel cell and electrolysis modes. Black and red curves show the results of St. Gobain cells with modified LSM and LSCF air electrode, respectively.

of a long-term test of the single cell with modified LSM air-electrode. The cell was operated galvanostatically at 0.5 A/cm^2 at 850 °C. The cell behaved very stable in the fuel cell mode with almost zero degradation. However, after switching to electrolysis mode, the cell started degrading rapidly. The test was shut down after 5 hours operation in the electrolysis mode.

More detailed information of degradation can be obtained from the impedance spectra. Impedance measurements were performed before the tests, between two tests, and after 5 hours operation in electrolysis mode. Fig. 13 shows the Nyquist plots of the impedance spectra. The intercept of the spectra at high frequency with real axis represents the ohmic resistance including electrolyte resistance. It illustrates that the electrolyte remains stable in electrolysis mode. The semi-circles at low

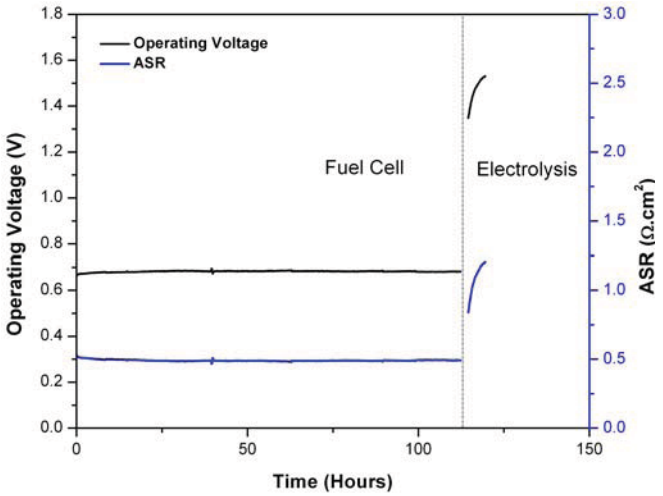

Figure 12. Long term test of St. Gobain #1 with modified LSM air-electrode. The cell is operated at 0. 5 A/cm^2 at 850 °C.

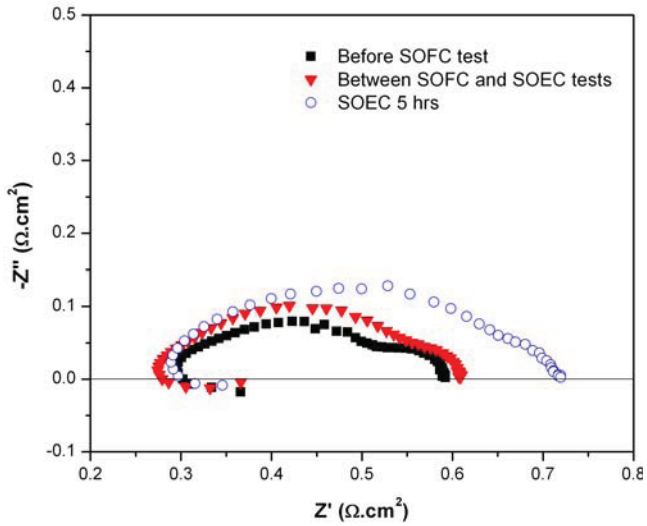

Figure 13. Nyquist plots of the impedance spectra measured during long term tests in fuel cell and electrolysis modes at open circuit conditions. The measurements are performed during the test shown in Fig. 12.

frequencies characterize the electrochemical behavior of the electrodes. It is seen that after operating in electrolysis mode for only 5 hours, the shape of semi-circle at low frequencies changes a lot. That means the electrodes degrade significantly after switching to electrolysis mode.

Fig. 14 shows the results of the long-term test of the single cell with LSCF air electrode. The cell is operated gavalostatically at 0.5 A/cm^2 at 850 °C. The cell was operated in fuel cell mode for 180 hours before switching to electrolysis mode. Significant degradation was found in electrolysis mode and the test was shut down after running in electrolysis mode for less than 10 hours. Visible delamination of the air-electrode was found in the post-test examination.

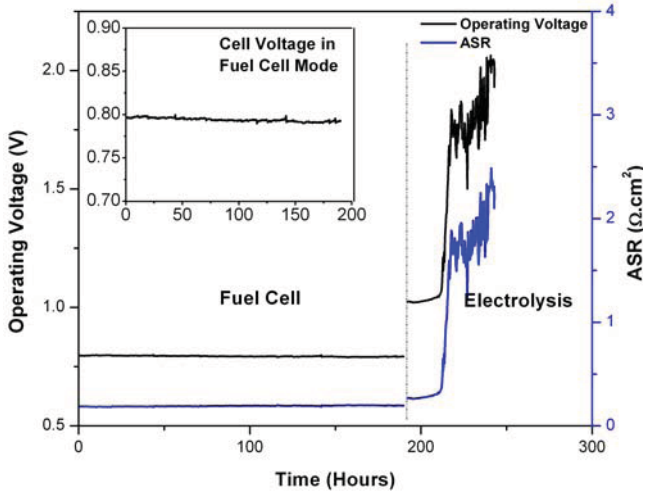

Figure 14. Long term test of St. Gobain #2 with LSCF air-electrode. The cell is operated at 0.5 A/cm^2 at 850 °C.

SUMMARY

A newly designed apparatus has been developed for testing of single solid oxide cells in both fuel cell and electrolysis modes of operation. Performance and durability evaluation of SOECs provided by MSRI, Ceramatec, and St. Gobain have been performed. MSRI SOECs demonstrated low degradation rates during durability tests at different current densities. One Ceramatec button cell was operated for 4000 hours and showed negative degradation. This exceptional performance was similar as that of one Ceramatec stack [13]. The reason caused the performance increase remains further investigation. St. Gobain single cells showed stable performance in the fuel cell mode, but experienced rapid degradation in the electrolysis mode. It further proves that SOFCs cannot be directly used for electrolysis. More cells will be tested at INL to investigate methods that can further mitigate degradation at single cell level.

ACKNOWLEDGMENTS

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